

X-ray Microprobe of Optical Strong-Field Processes

L. Young,^{a,*} R.W. Dunford,^a C. Hoehr,^a E.P. Kanter,^a B. Krässig,^a E.R. Peterson,^a S.H. Southworth,^a D.L. Ederer,^{a,†} J. Rudati,^b D.A. Arms,^b E.M. Dufresne,^b E.C. Landahl^b

^aChemistry Division, Argonne National Laboratory, Argonne, IL 60439, USA

^bAdvanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA

Elsevier use only: Received date here; revised date here; accepted date here

Abstract

A time-resolved x-ray microprobe to study optical strong-field processes has been developed. Individual atoms or molecules located within the strong-field environment created by a focused ultrafast laser are probed by undulator-produced x-ray pulses to achieve spatial, temporal, spectral and polarization selectivity. Approximately 10^6 monochromatic x-rays per 100-ps pulse are focused into a ~ 10 micron spot to selectively probe atoms in focal volumes where intensities up to 10^{15} W/cm² can be present. In this paper we describe the time-resolved x-ray microprobe and provide some illustrative examples from our work studying strong-field phenomena such as laser-modified absorption spectra, Coulomb explosion, transient laser-produced plasmas and molecular alignment. © 2001 Elsevier Science. All rights reserved

Keywords: X-ray, pump-probe, strong-field effects, synchrotron radiation, ultrafast x rays, microfocus x rays

1. Introduction

The study of structural dynamics on an ultrafast time scale is a prime motivation for the construction of large-scale next-generation x-ray sources, i.e. free electron lasers (XFELs), such as the Linac Coherent Light Source (Arthur, 2002) and the Tesla Test Facility (Tschentscher, 2004). These new sources will access the sub-picosecond timescale with very high single pulse fluence ($\sim 10^{13}$ x rays/200 fs pulse) in comparison with current synchrotron sources ($\sim 10^8$ x rays/100 ps pulse) and laser-produced plasma sources ($\sim 4 \times 10^6$ x rays/sr/100 fs pulse) (Bargheer, 2004). X-rays are particularly valuable in ultrafast dynamics research, since they provide complementary information to that available from optical and charged particle probes. X rays yield direct information on atomic positions and chemical bond lengths, unlike ultrafast optical probes (Zewail, 2003). X rays penetrate to probe isolated molecules in solution, buried interfaces and bulk

material response, unlike recently-developed ultrafast electron sources (Zewail, 2005; King et al., 2005; Siwick et al., 2003). In addition, tunable x rays from synchrotron sources provide chemical, elemental, and polarization specificity (Stohr, 1996). To this suite of synchrotron basics, one can add “ultrafast” temporal and “ultras-small” spatial information using the laser-pump/x-ray microprobe method described here, thus enabling new studies of the response of atoms and molecules to strong-optical fields.

Recently, there has been an explosion of activity at third-generation light sources using pump-probe techniques to track structural dynamics with ~ 100 picosecond x-ray pulses. These studies have been of solid-state materials ($\sim 10^{22}$ atoms/cm³) and solvated species ($\sim 10^{19}$ molecules/cm³). In ordered solid-state materials, phase-transitions and phonon propagation have been studied extensively, primarily using x-ray diffraction techniques (Sondhauss et al., 2005; DeCamp et al., 2003; Reis et al., 2001; Lindenberg et al., 2000). In some of these studies, the time resolution was extended below the x-ray pulse duration to the few ps level through the use of x-ray streak

*Corresponding author. Tel.: +1-630-252-8878; fax: +1-630-252-6210; e-mail: young@anl.gov.

†Permanent address: Tulane University, New Orleans, LA 70118, USA

cameras. Particularly noteworthy is the recent demonstration using ~ 100 femtosecond pulses from a laser-slicing source (Schoenlein et al., 2000) to study metal-insulator phase-transition dynamics with extended x-ray absorption techniques (Cavalleri et al., 2005). Studies of photoinduced structural dynamics of solute molecules have been done using both x-ray absorption spectroscopy (Chen et al., 2001; Saes et al., 2003) and x-ray diffraction (Neutze et al., 2001; Plech et al., 2004). Some recent achievements include the time-resolved study of chemical reactions and the isolation of a molecular transition state in solution by x-ray diffraction (Davidsson et al., 2005; Ihee et al., 2005). Access to the subpicosecond regime with hard x-rays has already started with experiments on crystal melting at the Sub-Picosecond Pulse Source (SPPS), the precursor to the LCLS (Lindenberg et al., 2005).

Our experiments, in contrast, focus on gas phase samples ($\leq 10^{14}$ cm³) with no long range order. Also in contrast to other pump-probe studies, we use strongly focused x-ray beams (~ 10 micron spot diameter). The combination of strongly-focused tunable x-rays with a strongly-focused ultrafast laser enables both the study of atomic and molecular response to strong-optical fields and an exploration of laser-induced modification of standard x-ray processes. In addition, gas phase studies are special in that x-ray interactions with isolated atoms and molecules are amenable to first-principles theory and will provide a solid foundation for pump-probe experiments with XFELs, where strong-optical fields are expected.

The response of atoms and molecules to strong-electromagnetic fields is of significant intrinsic interest. Within the past two decades, developments in ultrafast laser technology have powered revolutionary advances in the study of light-matter interactions at high-intensities (Brabec and Krausz, 2000). The diffraction-limited quality of the ultrafast laser pulses permits efficient focusing and thus with modest mJ pulse energies one can easily reach intensities of 10^{15} W/cm², corresponding to electric field strengths of ~ 10 V/Å. These external field strengths are comparable to those binding outer-shell electrons in an atom and manipulation of these electrons with strong-laser fields has led to the discovery of many fascinating phenomena, e.g. above threshold ionization (Agostini et al., 1987), high-harmonic generation (Salières et al., 1999) and molecular alignment (Stapelfeldt and Seideman, 2003). At higher intensities in the relativistic regime ($> 10^{16}$ W/cm²) there have been observations of laser-induced x-ray generation in clusters (McPherson et al., (1994), Ditmire et al., (1995)) and even nuclear fusion (Ditmire et al., 1999).

These experiments typically use a single intense laser pulse to irradiate a gas phase sample and analyze the products (electrons, ions, photons) to gain information on the interaction mechanisms. An independent, tunable ultrafast probe would add a valuable dimension to these studies, permitting the interrogation of state-specific atomic dynamics induced by the strong-field. Earlier studies

which use pump-probe techniques to study strong-field light-matter interactions have generally derived pump and probe pulses from the same laser, thus limiting both spectral tunability and pump-probe time delay range. In a pioneering experiment, Schins et al. made the first observation of laser-assisted Auger decay by using output from a single Ti:sapphire laser to provide both the “pump” IR dressing beam of $< 10^{12}$ W/cm² and the broadband “probe” x-rays generated from laser-irradiated liquid Ga (Schins et al., 1994). Subsequently, Glover et al. made the first observation of the laser-assisted photoelectric effect using an IR dressing beam combined with a family of high-harmonic probe beams within an energy range of 33-42 eV (Glover et al., 1996). In both cases, the Ti:sapphire lasers were multistage-amplified, low repetition rate, high pulse energy (10 Hz, ~ 40 -65 mJ). In these two experiments effect of the laser-dressing field is to cause free-free transitions in the continuum adding sidebands to the photoelectric or Auger peak in the electron energy spectrum. More recently, high harmonics have been used as probes of transient molecular alignment, (Kanai et al., 2005) again deriving the pump and probe from the same laser.

With the x-ray microprobe there are many advantages relative to pump-probe experiments derived from a single laser. First, spectral tunability: a probe x-ray beam derived from synchrotron radiation provides wide tunability (chemical and elemental sensitivity) and independent polarization control. Second, temporal tunability: independent control of the pump laser beam and the probe x-ray beam allows delay ranges from picoseconds to milliseconds. This enables the probing of properties of individual atoms and molecules at $t=0$ and probing of collective dynamics of the gas phase ensemble, e.g. Coulomb explosion, at later times. Third, microfocus advantages: the micron-sized x-ray beam allows both easy target replenishment with a flowing gas or liquid source to avoid sample damage, and, efficient use of laser pulse energy. For x-ray pulses of spot diameter d separated by time Δt a flow speed of only $d/\Delta t$ is needed to create a new target for each x-ray pulse; in our typical case $d=10$ microns, $\Delta t=150$ ns, the required flow velocity is only ~ 60 m/s. Finally, the efficient use of laser pulse energy gives access to high-field strengths with commercial high repetition-rate lasers. Indeed, it is possible to envision x-ray probing of laser-controlled reactions using currently-available frequency conversion systems having pulse energies of ~ 50 μ J throughout the IR to UV because only modest laser intensities $\sim 10^9$ W/cm² may be required.

In the following we describe the time-resolved x-ray microprobe, give some illustrative examples from our research and provide an outlook for the future development of atomic and molecular physics with time-resolved x-ray techniques.

2. The time-resolved x-ray microprobe

Figure 1 shows a schematic of the time-resolved x-ray microprobe at the Advanced Photon Source, Sector 7. X rays from an undulator are routed through a Si(111) double crystal monochromator to give a bandwidth of $\Delta E/E \sim 1.4 \times 10^{-4}$ and a flux of ~ 1 to 2×10^{13} photons/s. The source size and divergence of the x-rays give an unfocused spot size of $\sim 700 \mu\text{m} \times 2200 \mu\text{m}$ (V×H) FWHM at the experiment located ~ 58 m downstream from the source. We have chosen a 200-mm Kirkpatrick-Baez mirror pair (Eng et al., 1998) operated at ~ 4 mrad incidence angle to focus the x rays to $\sim 10 \mu\text{m}$ spot size in both dimensions while retaining 40% of the monochromatic flux! This corresponds to a $\sim 10^6$ x-rays per pulse that can be overlapped with a laser pulse. (Zone plates and refractive lenses commonly used in synchrotron research are less suited to our application which requires maximal flux, \sim micron-sized beams and longer, flexible focal distances for convenience. Zone plates give the optimal spot size 15 nm (Chao et al., 2005), but their aperture is limited, typically $\sim 100\text{-}\mu\text{m}$, and they must be refocused for different x-ray energies. Simple refractive lenses (Dufresne et al., 2001) typically produce spot sizes $\sim 50 \mu\text{m}$, too large for precise probing within the laser focus.) A beam position

monitor located between the monochromator and the experimental apparatus is used to stabilize the vertical position of the x-ray beam to $\pm 1 \mu\text{m}$ during a scan of the x-ray energy. Ion chambers and slits are placed at strategic locations to monitor and clean the x-ray beam.

The Ti:sapphire ultrafast laser system used to provide the strong-optical field is shown in the lower part of Figure 1. The oscillator runs at 88 MHz and is actively synchronized to the rf of the storage ring 352 MHz (Reis et al, 2001). The output of the oscillator is stretched, amplified and recompressed in a commercial regenerative amplifier (Coherent Legend HE-USP) pumped by a diode-pumped, intracavity-doubled Nd:YLF laser (Coherent Evolution-30). The compressed, amplified output has a central wavelength of ~ 800 nm, 2.5 W average power, pulse length ~ 45 fs, and a repetition rate that is variable from 1-5 kHz. The amplified output can also be diverted prior to the compressor to give chirped pulses of ~ 120 ps duration and ~ 3.5 W average power. The polarization of the laser beam can be either circular or linear with variable angle relative to the horizontally-polarized x-rays by insertion of waveplates. The laser enters the rear of the vacuum chamber and is focused into the interaction region with an in-vacuum spherical mirror, $f=100$ mm. Focusing at $f/10$ to $f/10$ is possible by varying the diameter of the

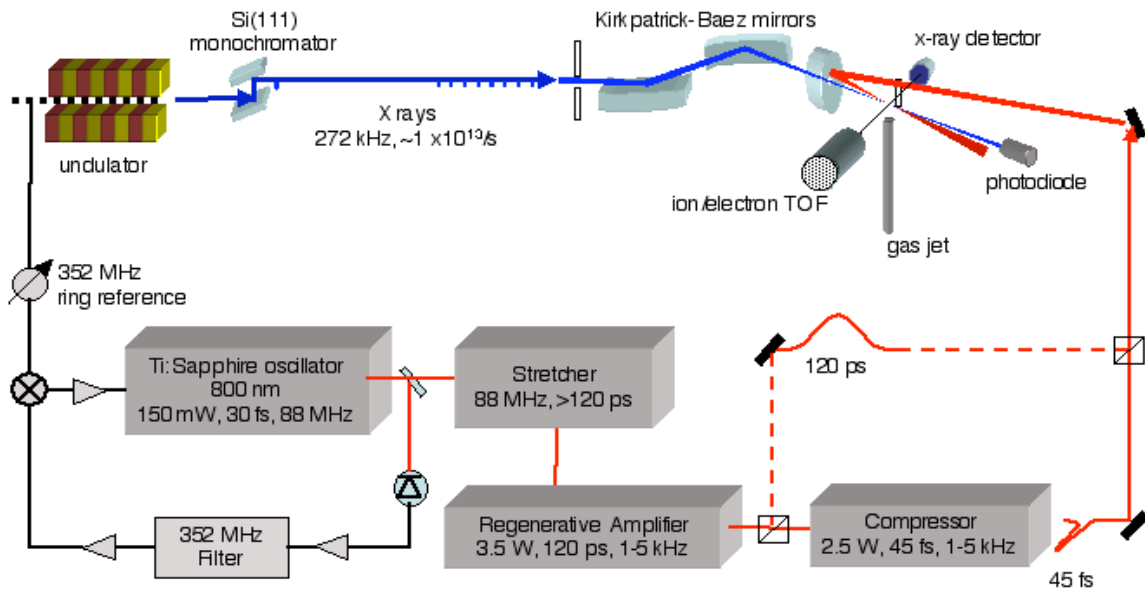


Fig. 1. Schematic of the time-resolved x-ray microprobe for atoms and molecules in the presence of strong-optical fields. Monochromatic x rays are focused with a Kirkpatrick-Baez mirror pair to ~ 10 micron spot size. The x rays probe within the interaction volume created by strong focusing of a Ti:sapphire laser with ~ 20 - 100 micron spot diameter. The interaction region is viewed by x-ray, ion and electron detectors. The target is an effusive gas jet at room temperature, with corresponding mean velocity of ~ 300 m/s for krypton.

input beam. A typical operating spotsize is $\sim 100 \mu\text{m}$ FWHM.

Overlapping the two focused beams, laser and x-ray, spatially and temporally within the gas jet inside a vacuum chamber is a demanding aspect of the experiment. The focused x rays enter the chamber through a hole in the center of the laser-focusing mirror and the two beams co-propagate through the interaction region. Rough spatial alignment at the interaction region is achieved with an *in situ* YAG scintillator screen observed with a lens system plus CCD camera (not shown in the figure). Fine alignment is done by scanning a $10\text{-}\mu\text{m}$ cross hair through the focal volume to map the laser and x-ray foci in x,y and z. The x-ray profile is monitored either by induced current from the cross hair or by transmission in a downstream ion chamber. The laser profile is simultaneously monitored by scatter into the lens/CCD camera setup. This method yields profile centroids to $\sim 2 \mu\text{m}$ precision.

Temporal overlap is also a multistep process. Rough overlap at the $\sim 0.5 \text{ ns}$ level is done with a photodiode downstream of the interaction region. The wings of the strongly divergent laser beam are sufficient to create a sizable response in the downstream photodiode that can be observed simultaneously with the x-ray beam. Refinement of the timing is done with cross-correlation measurements using Kr ionization as explained below. The jitter between the x-rays and the amplified laser output was measured on a shot-to-shot basis using the downstream and a laser-fiducial photodiode, constant fraction discriminators and a time-to-amplitude converter to be $\sim 3\text{ps}$.

A room temperature effusive gas jet forms the target at the interaction region. For atomic Kr, the mean velocity is $(1.33\sqrt{2kT/m}) \sim 300 \text{ m/s}$. This is sufficient to produce a new target for the arrival of each x-ray pulse. The width of the effusive jet at the interaction region was measured to be $\sim 2 \text{ mm}$ FWHM. For photon-in/photon-out spectroscopy, the interaction region is viewed by x-ray detectors (silicon drift detectors) that are capable of very high count rate and good energy resolution. The photon viewing region is limited to the central portion of the Rayleigh range by in-vacuum slits. The energy resolution of the detectors ($\sim 100 \text{ eV}$) is sufficient to discriminate scattering from fluorescence. Alternatively, the products of the laser/x-ray interaction can be viewed by ion/electron time-of-flight detectors or an energy-resolving cylindrical mirror analyzer (CMA). For the CMA the viewing region is limited by internal apertures. For time-of-flight spectroscopy, the position-sensitive detectors can be used to determine the location from which the ion originated.

The time structure of the Advanced Photon Source is an important consideration for laser pump/x-ray probe experiments because the two repetition rates are highly mismatched. The ring circulation period is $3.56 \mu\text{s}$ (272 kHz) The ring is run in top-off mode such that the average current is stabilized at $\sim 100 \text{ mA}$. The standard fill pattern has 24 equally-spaced pulses, each containing $\sim 4 \text{ mA}$,

separated by $\sim 153 \text{ ns}$. Significantly more current can be synchronized with the 1-5 kHz laser in the “hybrid-singlet” mode, where a superbunch containing up to 16 mA is isolated by symmetrical $1.59 \mu\text{s}$ gaps from 8 septets which distribute the remaining 84 mA . In addition, the long quiet period after the superbunch eases time-of-flight measurements and detector recovery. In the standard (hybrid singlet) case only $\sim 1/6800$ ($1/1700$) of the x-ray flux can be overlapped with a 1 kHz laser. Depending on the bunch current in the ring, the x-ray pulselength varies (Chae et al., 2001). The x-ray pulse duration in the standard (hybrid) mode is ~ 94 (153) ps FWHM.

3. Examples: Atoms and molecules in strong optical fields

3.1. Kr ionization – cross-correlation signature and ion spectroscopy

For 800 nm light, an intensity of $\sim 2 \times 10^{14} \text{ W/cm}^2$ is sufficient to saturate ionization of Kr (Maeda et al., 2000). This intensity is easily achievable with the existing laser system. If one saturates the ionization within the laser focal volume, then the x-rays will probe an ensemble of ions, thus enabling ion spectroscopy. There is a dramatic difference between the K-edge x-ray absorption spectrum of neutral and singly-ionized Kr as shown in Figure 2.

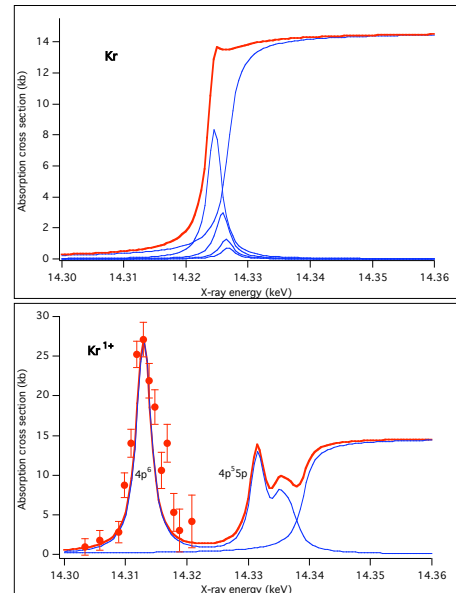


Fig 2. Top panel: Laser off: Calculated K-edge absorption spectrum of neutral Kr. Lower panel: Laser on: Calculated K-edge absorption spectrum of singly-ionized Kr. The red traces show the sum of the discrete and continuum components of the spectra, which are shown in blue. Preliminary data run show the strong resonance and are scaled to fit the calculated cross-section.

The large pre-edge feature in singly-ionized krypton corresponds to the $1s \rightarrow 4p$ resonance. Since this resonance appears only after laser-induced ionization and occurs in a region of “zero” absorption for the neutral, it is a very *clean* signature of laser/x-ray overlap. The theoretical ratio of the laser on/laser off signal when the x-rays are tuned to the $1s \rightarrow 4p$ resonance at 14.313 keV is ~ 40 . By detecting only the $K\alpha$ fluorescence channel, we isolate the K-shell absorption allowing us to observe the large laser on/laser off ratio. This ratio would be drastically decreased in a transmission measurement. The observed laser-on/laser-off ratio approaches the theoretical value and is used to optimize spatial/temporal overlap *in situ* during an experiment.

It is interesting to note that ion spectroscopy can be realized with the x-ray microprobe. The photon-in/photon-out technique permits the observation of isolated atom properties even at relatively high density. The localized gas density 1-2 mm from the nozzle can approach $\sim 10^{14}/\text{cm}^3$. Under saturation conditions, the ion density is also $\sim 10^{14}/\text{cm}^3$ over the extent of the gas jet $\sim 2\text{mm}$. (For a 100 μm beam FWHM, the beamwaist (w_0) = 60 μm , and the Rayleigh range of the laser focus $Z_r = \pi w_0^2/\lambda$ exceeds the extent of the gas jet.) With this ion sample, the target thickness is $\sim 10^{13}/\text{cm}^2$, far exceeding the target thickness in a collinear ion beam setup, where the ion density is typically limited by space charge to $\sim 10^7/\text{cm}^3$ and the interaction length to $\sim 100\text{cm}$.

The drawback in this scheme for ion spectroscopy scheme is the difficulty in selectively producing a single charge state with intense pulsed lasers. As one can see from the preliminary data shown in Figure 2 of the resonance region, the width of the resonance is greater than the theoretical lineshape, suggesting the presence of higher charge states. Indeed more extensive spectroscopic measurements combined with ion charge state measurements have confirmed the presence of Kr^{2+} . The higher charge state is formed in the central region of the laser focus. At these ion densities, the sample undergoes Coulomb expansion which segregates the charge states in time and space. Thus, with careful spatial and temporal placement of the x-ray microprobe, this problems associated with multiple charge state production can be overcome.

3.2. Coulomb expansion of transient laser-produced plasmas

The high ion density ($\sim 10^{14}/\text{cm}^3$) produced by laser ionization is accompanied by the production of electrons; this collection of ions and electrons form a transient independent particle plasma until the electrons leave the ion vicinity determined by the laser focus ($\sim 100\text{ }\mu\text{m}$). After the electrons leave, the ion assembly undergoes pure Coulomb expansion. In tunnel ionization, electrons are produced with a time-averaged kinetic energy of $U_p \propto \lambda^2 I = 0.94 \times 10^{-13} \lambda^2 I$ where I (W/cm^2) is the laser intensity and λ

(microns) is the laser wavelength and U_p is given in eV. For an intensity of $4 \times 10^{14} \text{ W}/\text{cm}^2$ with 800 nm radiation, this corresponds to a $U_p \sim 24 \text{ eV}$ ($v_e \sim 3 \text{ mm/ns}$). Neglecting electron recapture by the ion cloud, the electrons will leave the ion vicinity within a fraction of a nanosecond. However, electron recapture may not always be negligible with the presence of strong Coulomb attraction from the ionized core. Electron energy distributions can be controlled by varying the polarization of the strong-field ionization laser (Corkum et al., 1989) and the ensuing dynamics of the ion/electron cloud can be simulated and followed with the x-ray microprobe. Obvious extensions of the x-ray microprobe technique include the probing of dense laser-produced plasmas and laser-ablation mechanisms with spectroscopic, polarization, spatial and temporal selectivity.

3.3. Dressed atoms and molecules: Molecular alignment

There are many applications for aligned molecules, ranging from studies of photoionization of fixed-in-space molecules, enhanced high-harmonic generation, optimized chemical reactivity and simplified serial single molecule crystallography with next-generation sources. Alignment can be achieved with pulsed lasers, either adiabatically or impulsively. Adiabatic laser alignment (Friedrich and Hershbach, 1995) is simply an extension of static DC field alignment, where the molecule is aligned preferentially along the laser polarization axis due to interaction with its anisotropic polarizability. Two requirements for the adiabatic aligning laser pulses exist. The field strength that can be imposed is limited by the threshold for ionization, e.g. $\sim 10^{12} \text{ W}/\text{cm}^2$ for I_2 . The laser pulse length must be significantly longer than the molecular rotational period, $\tau_{\text{laser}} > \tau_{\text{rot}}$, for the alignment to evolve adiabatically. In the presence of the aligning field, the free rotor evolves into an eigenstate of the complete Hamiltonian, i.e. a “pendular” state. As the laser field decays, the alignment is lost.

In contrast, with the impulsive scheme, molecules are aligned *subsequent* to passage of a short laser pulse. The impulse coherently excites a superposition of rotational states to create an aligned ensemble that then decays and revives at predictable intervals (Seideman, 1999; Ortigoso et al., 1999). A full revival is observed to occur after a rotational period $T = 1/2Bc$ where B is the rotational constant of the molecule in cm^{-1} and c is the speed of light. Partial revivals occur at $T/4$, $T/2$, $3T/4$ (Rosca-Pruna and Vrakking, 2001). The revival duration is dependent upon the interplay between molecular and laser pulse parameters but typically lasts for no more than a few picoseconds. The advantage for many applications is that molecules are aligned under field-free conditions.

In order to study inner-shell photoionization from aligned molecules, one can use the x-ray microprobe to interrogate the aligned molecule. With the current pulse length at the Advanced Photon Source, $\sim 100 \text{ ps}$, it would

be impossible to interrogate the impulsively-aligned molecules. However, to probe adiabatically-aligned molecules, the alignment laser pulse must simply be longer than the x-ray pulse. This is possible with the current laser system by diverting the amplified output prior to recompression to achieve ~ 120 ps pulses, as shown in Figure 1 by the dashed line. Typically, adiabatic alignment is done with low repetition rate, 10 ns pulse length lasers. However, with microfocus conditions, adiabatic alignment at kHz repetition rates is feasible thus enabling studies of synchrotron-based x-ray photoionization from dressed atoms and molecules (i.e. aligned) with reasonable count rates.

4. Future outlook – 1-ps x rays at the Advanced Photon Source

While most of the applications discussed above can be realized with the presently-available bunch lengths from the Advanced Photon Source ~ 100 -ps FWHM, they would clearly benefit from shorter pulses of ~ 1 -ps duration. In addition to the 100-fold increase in time-resolution one also obtains a similar increase in accessible field strength for dressed-state and coherent control studies in atoms and molecules (Rice and Zhao, 2000).

An ingenious scheme to produce subpicosecond x-ray pulses in a storage ring was proposed in 1999 by Zholents and coworkers (Zholents et al., 1999). The basic concept is that a transversely-deflecting RF cavity in the storage ring structure can be used to create a vertical or angular displacement that is correlated with the longitudinal position within an electron bunch, i.e. a chirped electron bunch. A second cavity placed at a vertical phase advance $n\pi$ downstream of the first cancels the correlation. The transverse displacement can be made large enough such that the x-ray radiation from the bunch can be considered as a large number of independent sources, each of which would have a duration of ~ 1 ps. Ideally, only the section of the storage ring between the two cavities would have short pulses; the impact on the rest of the ring would be negligible. This concept has been intensively investigated over the past year at the Advanced Photon Source both in simulation by Borland (Borland, 2005) and in practice by Harkay and coworkers (Guo et al., 2005). The simulations show that the concept is practical and the test beam studies confirm the accuracy of the simulation parameters. The source parameters are currently being refined, and recently it has been discovered that an early concern, vertical emittance growth throughout the ring (Borland, 2005), can be largely eliminated, even at the high deflection voltage needed for the shortest pulses (Borland and Sajaev, 2005a).

The availability of a high-repetition rate, short-pulse x-ray source will vastly increase the current parameter space available for time-resolved x-ray studies. Table 1 lists working parameters for the APS storage ring and the

specifications for the LCLS XFEL. The parameters for the simulated 1-ps storage-ring source are shown in parentheses in the second column. For the LCLS, parameters for two modes are shown, the 8000 eV mode and the 800 eV mode in parentheses. Although the expected pulse duration is ~ 5 -fold longer than initial specifications at LCLS, the average power is similar and there are a number of advantages of the storage ring rf deflection method namely: a high-repetition rate 6.5 MHz vs 120 Hz; modest fluence 10^8 x-rays per pulse (for reduced sample damage and suitability for time-resolved probes) vs high fluence 10^{12} x-rays per pulse; well-characterized temporal and energy profiles vs chaotic profiles with large shot-to-shot variation; simultaneous users at multiple wavelengths vs single users; existing detector and signal processing techniques vs required development of single-shot techniques and advanced detectors.

A practical issue is the relatively large vertical beamsizes of the chirped x-ray pulse. The angular deflection correlates with time at a slope of ~ 380 $\mu\text{rad}/40$ ps rms pulse in the APS storage ring. Thus, at the location of the x-ray optics, 30 m downstream, a vertical beamsize of ~ 11 mm for the chirped x-ray pulse is formed. A simple sub-mm slit at this position could yield a pulse length of a few ps FWHM. This slitted beam could be used for spectroscopy in energy-dispersive mode (Pettifer et al., 2005) to accumulate an x-ray spectrum over the entire undulator bandwidth in transmission mode with ~ 1 ps resolution. In addition, many condensed matter diffraction experiments are not photon-limited, and the simple slit would greatly improve the time-resolution achievable. It is also possible to use asymmetrically cut crystals and mirrors to compress the x-ray pulse in both time and space and increase the flux ~ 10 -fold over that achieved by simple slitting at the same pulse duration (Shastri, 2005). Thus, it is reasonably straightforward to advance to the 1-ps timescale using a storage-ring-based source coupled with existing technology.

As a complement to the chirped-pulse storage ring concept, XFELs produce the shortest pulse duration and highest intensity in the hard x-ray region. Indeed, XFEL enhancement schemes based upon emittance spoiling (Emma et al., 2004) and further phase space manipulation of the electron beam (Zholents and Fawley, 2004) suggest that pulses of few femtosecond and even attosecond duration are possible! Initial experiments with baseline parameters at the XFEL must diagnose XFEL output which will have pulse-to-pulse fluctuations in temporal (and hence spectral) profiles since the SASE lasing process is initiated from noise. Atomic and molecular physics is expected to play a key role here as the simplicity of the target permits close coupling of *ab initio* theory with experiment to understand strong-field interactions at short-wavelengths.

Table 1. Comparison of APS vs LCLS x-ray sources. APS photon beam parameters are given for Undulator A (Dejus et al, 2002). LCLS photon beam parameters from LCLS Conceptual Design report (Arthur et al., 2002).

Parameter	APS storage ring	LCLS XFEL
Pulse duration FWHM	~100 ps (1.5 ps)	<230 fs
Repetition rate	6.5 MHz	120 Hz
Photons/pulse	$\sim 10^8$	$\sim 1.1 \times 10^{12}$ ($\sim 2.8 \times 10^{13}$)
Photon energy	~3-35 keV	~8.2(0.82) keV
Energy bandwidth	$\sim 10^{-2}$	0.06(0.24)%
Beam size	$254 \times 12 \mu\text{m}$	$28 \mu\text{m} \sigma_{\text{rms}}$
$\sigma_x \times \sigma_y$	$(245 \times 12 \mu\text{m})$	$(31 \mu\text{m})$
Beam divergence	$15.6 \times 3.0 \mu\text{rad}$	$0.43 \mu\text{rad} \sigma_{\text{rms}}$
$\sigma_x' \times \sigma_y'$	$(12.3 \times 2.2 \mu\text{rad})$	$(3.8 \mu\text{rad})$
Temporal profile	Gaussian	Chaotic
Spectral profile	Smooth	Chaotic

5. Summary

X-ray microprobe techniques can be particularly advantageous for time-resolved studies via pump-probe techniques. In particular, microfocused x-rays can probe focal volumes where laser intensities of up to $\sim 10^{15} \text{ W/cm}^2$ can be present using a commercial regeneratively-amplified Ti:sapphire laser system. The full power of tunable-synchrotron radiation then allows the detailed probing of strong-field-induced processes, e.g. the Coulomb expansion dynamics of an independent particle plasma produced by tunnel ionization in a gas and the tunnel ionization process itself. The efficient utilization of available laser power via microfocusing permits the study of molecular alignment at kHz repetition rates, making such experiments feasible in a storage ring environment. Finally, the generation of ~1-ps x-ray pulses at the Advanced Photon Source appears to be practical, enhancing both the temporal resolution and attainable dressing-intensity 100-fold and enabling exciting new science.

Acknowledgements

We thank P. Eng for the loan of Kirkpatrick-Baez mirrors. We also thank D.A. Reis, M. DeCamp, R. Crowell and D. Gozstola for early assistance with the laser system and D. Walko, B. Adams for beamline assistance at Sector 7 of the Advanced Photon Source. This work was supported in part by the Chemical Sciences, Geosciences, and Biosciences Division and the Advanced Photon Source by the Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, under Contract No. W-31-109-Eng-38.

References

- Agostini, P., Fabre, F., Mainfray, G., Petite, G. and Rahman, N. K., 1987. Free-free transitions following six-photon ionization of xenon atoms, *Phys. Rev. Lett.* 42, 1127.
- Arthur, J. *et al.*, 2002. Linac Coherent Light Source (LCLS) Conceptual Design Report. SLAC-R-593.
- Bargheer, M., Zhavoronkov, N., Gritsai, Y., Woo, J.C., Kim, D.S., Woerner, M., Elsaesser, T., 2004. Coherent Atomic Motions in a Nanostructure Studied by Femtosecond X-ray Diffraction. *Science*, 306, 1771-1773.
- Borland, M., 2005. Simulation and analysis of using deflecting cavities to produced short x-ray pulses with the Advanced Photon Source. *Phys. Rev. ST Accel. Beams*, 8, 074001-1-074001-18.
- Borland, M. and Sajaev, V., 2005a. Simulations of x-ray slicing and compression using crab cavities in the Advanced Photon Source. *Proc. 2005 Particle Accelerator Conf. (PAC)*, Knoxville, TN, in press.
- Brabec, T. and Krausz, F., 2000. Intense few-cycle laser fields, *Rev. Mod. Phys.* 72, 545-591.
- Cavalleri, A., Rini, M., Chong, H.H.W., Fourmaux, S., Glover, T.E., Heimann, P.A., Kieffer, J.C., and Schoenlein, R.W., 2005. Band-Selective Measurements of Electron Dynamics in VO₂ Using Femtosecond Near-Edge X-Ray Absorption. *Phys. Rev. Lett.* 95, 067405-1-067405-4.
- Chae, Y.-C., Emery, L., Lumpkin, A.H., Song, J. and Yang, B.X., 2001. Measurement of the longitudinal microwave instability in the APS storage ring. *Proceedings of the Particle Accelerator Conference, Chicago, Illinois, 2001* (IEEE, Piscataway, New Jersey), 1817-1819.
- Chao, W., Harteneck, B.D., Liddle, J.A., Anderson, E.H., Attwood, D.T., 2005. Soft X-ray microscopy at a spatial resolution better than 15 nm. *Nature* 435, 1210-1213.
- Chen, L.X., Jäjer, W.J.H., Jennings, G., Gosztola, D.J., Munkholm, A., Hessler, J.P., 2001. Capturing a Photoexcited Molecular Structure Through Time-Domain X-ray Absorption Fine Structure. *Science* 292, 262 - 264.
- Corkum, P. B., Burnett, N.H., and Brunel, F., 1989. Above-Threshold Ionization in the Long-Wavelength Limit. *Phys. Rev. Lett.* 62, 1259-1262.
- Davidsson, J., Poulsen, J., Cammarata, M., Georgiou, P., Wouts, R., Katona, G., Jacobson, F., Plech, A., Wulff, M., Nyman, G., Neutze, R., 2005. Structural Determination of a Transient isomer of CH₂I₂ by Picosecond X-Ray Diffraction. *Phys. Rev. Lett.* 94, 245503-1-245503-4.
- DeCamp, M.F., Reis, D.R., Cavalieri, A., Bucksbaum, P.H., Clarke, R., Merlin, R., Dufresne, E.M., Arms, D.A., Lindenberg, A.M., MacPhee, A.G., Chang, Z., Lings, B., Wark, J.S., Fahy, S. 2003. Transient Strain Driven by a Dense Electron-Hole Plasma. *Phys. Rev. Lett.* 91, 165502-1-165502-4.
- Dejus, R., Vasserman, I.B., Sasaki, S., Moog, E.R., 2002. Undulator A Magnetic Properties and Spectral Performance. *ANL/APS/Technical Bulletin-45*, 1-51.
- Ditmire, T., Donnelly, T., Falcone, R.W., and M.D. Perry, 1995. Strong x-ray emission from high-temperature plasmas produced by intense irradiation of clusters, *Phys. Rev. Lett.* 75, 3122-3125.
- Ditmire, T., Zweiback, J., Yanovsky, V.P., Cowan, T.E., Hays, G., Wharton, K.B., 1999. Nuclear fusion from explosions of

- femtosecond laser-heated deuterium clusters, *Nature* 398, 489-491.
- Dufresne, E.M., Arms, D.A., Clarke, R., Pereira, N.R., Dierker, S.B., Foster, D., 2001. Lithium metal for x-ray refractive optics., *Appl. Phys. Lett.* 79, 4085-4087.
- Emma, P., Bane, K., Cornacchia, M., Huang, Z., Schlarb, H., Stupakov, G., and Walz, D., 2004. Femtosecond and Subfemtosecond X-ray Pulses from a Self-Amplified Spontaneous-Emission-Based Free-Electron Laser. *Phys. Rev. Lett.* 92, 074801-1– 074801-4.
- Eng, P.J., Newville, M., Rivers, M.L., Sutton, S.R., 1998. Dynamically Figured Kirkpatrick Baez X-ray Micro-Focusing Optics. *SPIE Proc.* 3449, 36-47.
- Friedrich, B. and Herschbach, D., 1995. Alignment and Trapping of Molecules in Intense Laser Fields. *Phys. Rev. Lett.* 74, 4623-4626.
- Glover, T.E., Schoenlein, R.W., Chin, A.H., and Shank, C.V., 1996. Observation of laser assisted photoelectric effect and femtosecond high order harmonic radiation, *Phys. Rev. Lett.* 76, 2468-2471.
- Guo, W., Borland, M., Harkay, K., Sajaev, V., Yang, B., 2005. Generating Picosecond X-ray Pulses with Beam Manipulation in Synchrotron Light Sources. *Proc. 2005 Particle Accelerator Conf. (PAC)*, Knoxville, TN, in press.
- Ihee, H., Lorenc, M., Kim, T.K., Kong, Q.Y., Cammarata, M., Lee, J.H., Bratos, S., Wulff, M., 2005. Ultrafast X-ray Diffraction of Transient Molecular Structures in Solution. *Science* 309, 1223-1227.
- Kanai, T., Minemoto, S. and Sakai, H., 2005, Quantum interference during high-order harmonic generation from aligned molecules, *Nature*, 435, 470-474.
- King, W.E., Campbell, G.H., Frank, A., Reed, B., Schmerge, J.F., Siwick, B.J., Stuart, B.C., Weber, P., 2005. Ultrafast electron microscopy in materials science, chemistry and biology, *J. Appl. Phys.* 97, 111101.
- Lindenberger, A. M., Kang, I., Johnson, S.L., Missalla, T., Heimann, P.A., Chang, Z., Larsson, J., Bucksbaum, P.H., Kapteyn, H.C., Padmore, H.A., Lee, R.W., Wark, J.S., Falcone, R.W., 2000. Time-Resolved X-ray Diffraction from Coherent Phonons during a Laser-Induced Phase Transition. *Phys. Rev. Lett.* 84, 111-114.
- Lindenberger, A., et. al., 2005. Atomic Scale Visualization of Inertial Dynamics. *Science* 308, 392-395.
- Maeda, H., Dammasch, M., Eichmann, U., Sandner, W., Becker, A., Faisal, F.H.M., 2000. Strong-field multiple ionization of krypton. *Phys. Rev. A* 62, 035402-1–035402-4.
- McPherson, A., Thompson, B.D., Borisov, A.B., Boyer, K. and Rhodes, C.K., 1994, *Nature* 370, 631-634.
- Neutze, R., Wouts, R., Techert, S., Davidson, J., Kocsis, M., Kirrander, A., Schotte, F., Wulff, M., 2001. Visualizing Photochemical Dynamics in Solution through Picosecond X-Ray Scattering. *Phys. Rev. Lett.* 87, 195508-1 – 195508-4.
- Ortigoso, J., Rodríguez, M., Gupta, M., Friedrich, B., 1999. Time evolution of pendular states created by the interaction of molecular polarizability with a pulsed nonresonant laser field. *J. Chem. Phys.* 110, 3870-3875.
- Pettifer, R.F., Mathon, O., Pascarelli, S., Cooke, M.D., Gibbs, M.R.J., 2005. Measurement of femtometre-scale atomic displacements by X-ray absorption spectroscopy. *Nature* 435, 78-81.
- Plech, A., Wulff, M., Bratos, S., Mirloup, F., Vuilleumier, R., Schotte, F., and Anfinrud, P.A., 2004. Visualizing Chemical Reactions in Solution by Picosecond X-Ray Diffraction. *Phys. Rev. Lett.* 92, 125505-1 – 125505-4.
- Reis, D.A., DeCamp, M.F., Bucksbaum, P.H., Clarke, R., Dufresne, E., Hertlein, M., Merlin, R., Falcone, R., Kapteyn, H., Murnane, M.M., Larsson, J., Missalla, Th., Wark, J.S., 2001. Probing Impulsive Strain Propagation with X-ray Pulses. *Phys. Rev. Lett.* 86, 3072-3075.
- Rice, S.A. and Zhao, M. 2000. *Optical Control of Molecular Dynamics* (Wiley, New York).
- Rosca-Pruna, F. and Vrakking, M.J.J., 2001. Experimental Observation of Revival Structures in Picosecond Laser-Induced Alignment of I₂. *Phys. Rev. Lett.* 87, 153902-1–153902-4.
- Saes, M., Bressler, C., Abela, R., Grollmund, D., Johnson, S.L., Heimann, P.A., Chergui, M., 2003. Observing Photochemical Transients by Ultrafast X-Ray Absorption Spectroscopy. *Phys. Rev. Lett.* 90, 047403-1 – 047403-4.
- Salières, P. L’Huillier, A., Antoine, P., Lewenstein, M., 1999. Study of the spatial and temporal coherence of high-order harmonics, *Adv. At. Mol. Phys.*, 41, 83-142.
- Schins, J.M., Breger, P., Agostini, P., Constantinescu, R.C., Muller, H.G., Grillon, G., Antonetti, A., Mysyrowicz, A., 1994. Observation of Laser-Assisted Auger Decay in Argon. *Phys. Rev. Lett.* 73, 2180-2183.
- Schoenlein, R.W., Chattopadhyay, S., Chong, H.H.W., Glover, T.E., Heimann, P.A., Shank, C.V., Zholents, A.A., and Zolotarev, M.S., 2000. Generation of Femtosecond Pulses of Synchrotron Radiation. *Science*, 287, 2237-2240.
- Seideman, T., 1999. Revival Structure of Aligned Rotational Wave Packets. *Phys. Rev. Lett.* 83, 4971-4974.
- Shastri, S., 2005. private communication.
- Siwick, B., Dwyer, J.R., Jordan, R.E., Miller, R.J.D., 2003. An atomic-level view of melting using femtosecond electron diffraction. *Science* 302, 1382-1385.
- Sondhauss, P., Larsson, J., Harbst, M., Naylor, G.A., Plech, A., Scheidt, K., Synnergren, O., Wulff, M., Wark, J.S., 2005. Picosecond X-Ray Studies of Coherent Folded Acoustic Phonons in a Multiple Quantum Well. *Phys. Rev. Lett.* 94, 125509-1–125509-4.
- Stapelfeldt, H. and Seideman, T., 2003. Aligning molecules with strong laser pulses, *Rev. Mod. Phys.* 75, 543-556.
- Stöhr, J., 1996. *NEXAFS Spectroscopy*, Springer, Berlin.
- Tschentscher, Th., 2004. Investigation of ultrafast processes using X-ray free-electron laser radiation. *Chem. Phys.* 299, 271-276.
- Zewail, A., 2003. Nobel Lectures, Chemistry 1996-2000, Ed. Grenthe, I., World Scientific, Singapore, 274-367.
- Zewail, A., 2005. Diffraction, crystallography and microscopy beyond three dimensions, structural dynamics in space and time, *Phil. Trans. Royal Soc. A* 364, 315-329.
- Zholents, A., Heimann, P., Zolotarev, M., and Byrd, J., 1999. Generation of subpicosecond X-ray pulses using RF orbit deflection. *Nucl. Instrum. Methods Phys. Res., Sect. A* 425, 385-389.
- Zholents, A.A. and Fawley, W.M., 2004. Proposal for Intense Attosecond Radiation from an X-ray Free-Electron Laser. *Phys. Rev. Lett.* 92, 224801-1–224801-4.